

## Structural memory effect in solid-state transformation of kinetic coordination networks

The chemistry of porous coordination networks has shown a rapid advance in the last 15 years owing to the hybrid nature of their building blocks (i.e., metal ions and organic ligands) [1]. The selective synthesis of kinetic over thermodynamic products is an important aspect in porous coordination networks. In general, kinetic or thermodynamic structures can be prepared by fast or slow crystallization methods, respectively. However, synthetic routes enabling such selectivity as homogeneous products are not trivial. Fast precipitation can generate metastable products but as microcrystals that are not suitable for single-crystal X-ray analysis. We have recently demonstrated that “instant synthesis” can form kinetic microcrystalline porous coordination networks suitable for *ab initio* XRPD structure determination [2] and how new porous structures could be obtained by the annealing of kinetic products [3].

Herein, we studied a kinetically controlled family of isostructural porous coordination networks  $[(\text{ZnX}_2)_3(\text{TPT})_2]_n \cdot 5.5(\text{solvent})$  (where  $X = \text{I}, \text{Br}, \text{and Cl}$ ), where TPT is tris(4-pyridyl)triazine (**1-3**) (Fig. 1) obtained by “instant synthesis” and studied its solid-state reactivity at high temperatures (above 573 K). Insights on the solid-state reactions were obtained using state-of-the-art methods for *ab initio* XRPD structure determination by synchrotron X-ray diffraction at **BL19B2** and **BL02B2** beamlines [4].

Upon heating from 300 to 673 K, network **1** undergoes a crystalline-to-amorphous-to-crystalline (CAC) phase transition. *In situ* XRPD shows that **1**

changes to an amorphous phase at 473 K, and upon further heating, a new crystalline porous phase (**1a**) appears uniformly at 573 K and is stable up to 673 K (Fig. 1). We demonstrated the guest inclusion ability of **1a** by immersing it in nitrobenzene and exposing **1a** to  $\text{I}_2$  vapor. *Ab initio* XRPD structure determination (BL19B2 beamline) indicated that **1a** can reversibly encapsulate nitrobenzene [3] and  $\text{I}_2$  [4].

The CAC reaction in **1** involves the guest removal and concurrent shrinking of the networks, followed by the unlocking of interpenetrated networks (cleavage of coordination bonds), and crystallization by bond formation to yield **1a** (Fig. 2).

To test if the molecular prearrangement in **1** is necessary for the formation of **1a**, we performed control experiments by mixing, grinding, and heating using the same stoichiometric amounts of starting materials of **1** as in instant synthesis. X-ray analysis proved that **1a** was not formed (Fig. 2).

Intrigued by the results, we investigated the isostructural networks **2** and **3**. Microcrystalline **2** was heated to 573 K and monitored by *in situ* XRPD analysis. The diffraction data shows also two phase transitions through a CAC process. Elemental analysis results suggest the formation of the compound  $[(\text{ZnBr}_2)_3(\text{TPT})_2]_n \cdot (\text{H}_2\text{O})$  (**2a**). The high quality synchrotron XRPD data of **2a** was recorded at BL19B2 and structure determination was carried out by *ab initio* XRPD followed by Rietveld refinement (Fig. 3) [4]. Compound **2a** is an interpenetrated network obtained after guest removal and molecular

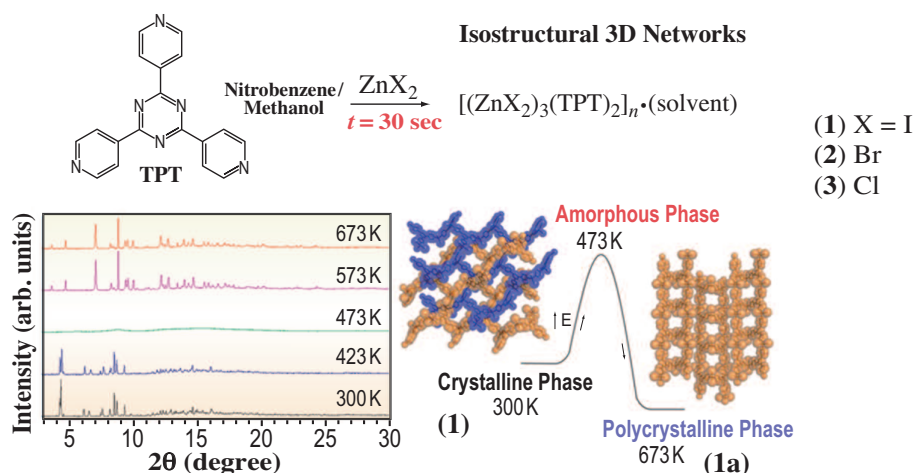
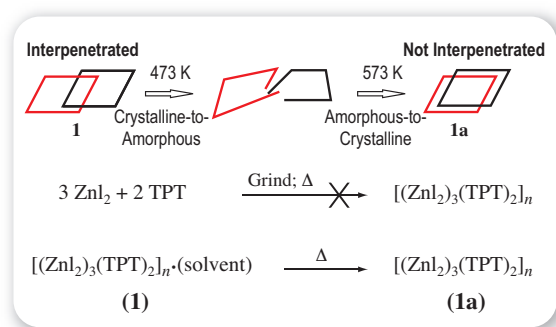


Fig. 1. Top: Fast crystallization of **1-3** by the “instant synthesis” method. Bottom: XRPD of **1** measured at different temperatures (left). Crystal structures of **1** and **1a** and energy plot depicting the transformation from kinetic to thermodynamic products upon heating via an amorphous phase. Interpenetrating networks are shown in blue and orange (right).



**Fig. 2.** Top: Cartoon showing the structural transformation from **1** to **1a**. Middle: control experiments showed that it is not possible to obtain the porous network **1a** if the building blocks ( $\text{ZnI}_2$  and TPT) are mixed, grinded, and heated. Bottom: the molecular prearrangement in **1** is necessary to form **1a**, which is only formed upon heating.

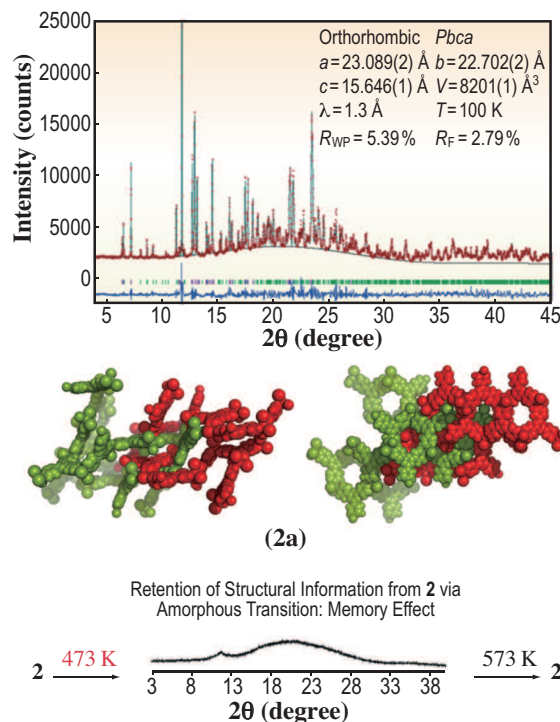
rearrangement (Fig. 3). To determine whether the unlocking of networks occurs, we investigated a non-interpenetrated (**2b**) network (not shown here, see Ref. [4]) with the same chemical composition of **2**. Heating **2b** to 553 K yields the same XRPD pattern and therefore the crystal structure of **2a** [4]. Clearly, the cleavage and formation of coordination bonds occur during the CAC transformation from non-interpenetrated (**2b**) to interpenetrated (**2a**).

Control experiments performed by mixing the starting materials using the same stoichiometry and grinding followed by annealing did not form **2a**, indicating that the atomic-level preorganization in the starting solids is crucial for the formation of the structures obtained after annealing. To our understanding, in the amorphous phase, structural information is retained and is passed via a type of memory effect from metastable (**2**) to a more stable (**2a**) (Fig. 3, bottom).

Further heating to 723 K and slow cooling of **2** produced single crystals with a new bromide-bridged network. In this case, the high temperature induced a certain level of calcination and, most likely, partial melt of **2** allowed crystallization upon slow cooling. A similar behavior was observed for the chloride version **3** (see Ref. [4]), which also through a CAC process formed a new phase (nonporous desolvated structure) that was unstable; thus, it transformed to a new chloride-bridged network at 723 K. The different solid-state reactivity can be attributed to the different halides in **1-3**.

In summary, we demonstrated that the frequently observed limitation in the single-crystal X-ray analysis of crystalline solids with good crystallinity and size has been tackled using a state-of-the-art *ab initio* synchrotron XRPD structure solution. In a type of memory effect, the amorphous phase in the CAC

process is an intermediate state retaining structural information from the kinetic structure that is passed to a more stable structure upon heating. Clearly, such a detailed structural analysis of organic-inorganic materials is trivial in single-crystal X-ray analysis but not in *ab initio* XRPD analysis.



**Fig. 3.** Top: Experimental (red), calculated (pale-blue), and difference (dark-blue) XRPD profiles from the final Rietveld refinement of **2a**. Middle: crystal structure of **2a** with the two interpenetrated circuits in green and red (side view) and viewed along the *c*-axis (right). Bottom: XRPD showing the amorphous phase upon heating **2** and formation of **2a**. The very broad “peaks” indicate that the long-range order allows the passing of structural information from **2** to **2a**.

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